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A cyanate ester/microcapsule system with low cure temperature and self-healing capacity

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ABSTRACT

Microcapsules filled with epoxy resin were blended into cyanate ester resin to produce systems with low cure temperature and self-healing capacity. A 4,4′-diaminodiphenylsulfone (DDS) curing agent was adopted for the systems. The mechanical properties, thermal stability and self-healing ability of the system cured at low temperature were investigated. Cyanate ester systems with 2.5 wt% and 5.0 wt% microcapsules (MCs) demonstrated an 11–43% increase in fracture toughness (K_{IC}) relative to the neat resin cured at high temperature, and exhibited slightly lower thermal stability than the neat resin. The self-healing ability of cyanate ester with MCs was influenced by MC content and healing temperature, although for a formulation with 5.0 wt% MCs, recovery of 85% of the original fracture toughness was achieved by heat treatment of fractured samples for 1 h at 220 °C.

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1. Introduction

Cyanate ester (CE) resins are important high-temperature thermosetting polymers. The cured CE polymers exhibit high strength, low dielectric constants and dissipation factors, radar transparency, low water absorption, and superior metal adhesion. Because of these characteristics, they are well-suited for use in electrical components, aerospace structures, adhesives and functional materials [1–5]. However, the CE polymer is inherently brittle and prone to microcracking under service loads. When subjected to cyclic thermo-mechanical loading, the microcracks compromise the structural integrity of CE-based composites because of fiber/matrix debonding and inter-ply delamination [6–11].

Various approaches can be employed to improve the fracture toughness of CE formulations. The approaches include addition of high-thermoplastic tougheners [12–14], rubber inclusions [15–18], inorganic or organic fillers [19–23], thermosetting resins [24,25], and flexible molecules [26–28]. However, these methods are largely ineffective in restoring strength to cracked or damaged material. In such cases, localized damage is commonly repaired by plug/patch and scarf repairs, bolted plates and injecting resins [29–31], although these methods often cause new problems by altering the local stiffness, introducing local stress concentrations (e.g., from mechanical fasteners), and adding weight to the structure.

An alternative approach to repair involves the addition of polymeric microcapsules (MCs) containing a healing agent released when the MCs are ruptured by growing cracks. The addition of appropriate MCs can provide self-healing functionality and increase fracture toughness when the damage is caused by service loads [32–34]. Investigations of self-healing thermosetting materials have focused primarily on the effectiveness of self-healing in different polymers or composites fabricated at relatively low temperatures, and these studies have demonstrated benefits to both fracture toughness and the self-healing ability of epoxy resins [32–35].

In previous work, we developed systems comprised of CE resin filled with MCs, and showed that judicious additions of MCs improved mechanical properties [36]. However, MCs contents above 5.0 wt% significantly decreased the thermal decomposition temperature of the cured CE, an observation was attributed to the lower thermal stability of the MCs [36]. To design formulations for specific applications, chemists must first optimize the properties of the components of these smart materials. To date, few studies have evaluated the use of poly(urea–formaldehyde) (PUF) microcapsules filled with epoxy resins (PUF/EP MCs) as self-healing agents for high-temperature CE resins.

In this paper, we report the design and characterization of a high performance self-healing CE system with MCs (designated

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CE/MCs) that can be processed at low temperature (⩽180 °C). Small amounts of MCs were blended into the CE resin to minimize the influence on the thermal stability of the CE matrix, and 4,4′-diaminodiphenylsulfone (DDS) catalyst was used in the CE formulation to decrease the polymerization reaction temperature, thus ensuring a low cure temperature. The DDS catalyst also served as a curing agent for epoxy resin released from the MCs.

2. Experimental

2.1. Materials

For MC shell materials, a formulation of urea (U) and 37 wt% formaldehyde (F) was selected (Mauinckrodt Chemicals Advantor Performance Materials Inc.), and triethanolamine (TEA) was used to control the solution pH (Alfa Aesar). Analytical grade DDS was selected as catalyst (Alfa Aesar). Industrial grade CE resin (bisphenol A dicyanate (2,2′-bis(4-cyanatophenyl)isopropylidene, 98% pure, molecular weight: 278) were acquired (Zhejiang Shangyu Shengda Biochemical Co. Ltd., China), and bisphenol A epoxy resin (EP) was selected (Henkel). PUF/EP MCs were prepared following a specific protocol [37]. Fig. 1 shows the morphologies of PUF/EP MCs. The MCs are 5~150 μm, and the mean diameter is ~80 μm. The epoxy content of the MCs was ~82% (by weight), the thermal decomposition temperature (T_d: temperature at 5% weight loss) of the MCs was ~213 °C. Fig. 2 shows the chemical structures of the main materials.

2.2. Preparation of CE/MCs

To prepare the formulations, the CE resin was heated to 100 °C. After melting to a clear liquid, 1 wt% DDS was added. The temperature was raised to 120 °C and held for 30~40 min while stirring, then PUF/EP MCs (2.5 wt% and 5.0 wt%) were added and the mixture was stirred for an additional 10~20 min. Afterward, the mixture was poured into a pre-heated mold, degassed, and cured according to the following schedule: 130 °C/2 h + 150 °C/2 h + 180 °C/2 h. The cure schedule used for the neat CE was 150 °C/2 h + 180 °C/2 h + 200 °C/2 h, followed by a post-cure at 220 °C for 4 h. After curing, samples were cooled slowly to room temperature.

2.3. Characterization

Fourier transform infrared (FTIR) spectroscopy was performed by scanning KBr discs of the samples (Nicolet, ThermoScience), and differential scanning calorimetry (DSC) experiments were performed (Q2000, TA Instruments) at a heating rate of 10 °C/min in a nitrogen atmosphere, heating from 30 to 350 °C.

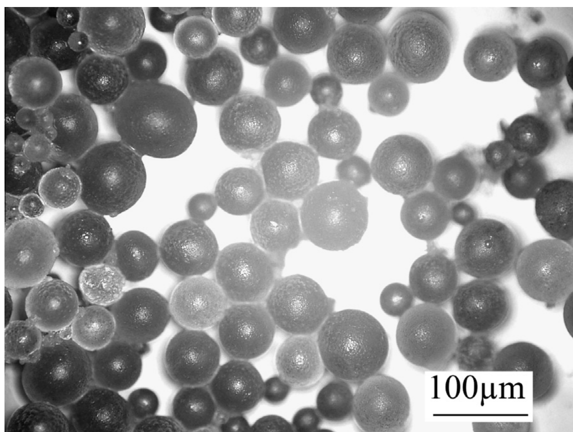

Fig. 1. Spherical PUF/EP MCs.

Flexural properties were evaluated using a load frame (Instron 4045). The three-point bend fixture featured contact points with a 5 mm radius of curvature. Tests were conducted at 25 °C using a cross-head speed of 0.5 mm/min, and 10~15 specimens per composition were tested. The flexural strength, σ_f was calculated using following equation:

$$\sigma_f = \frac{3FS}{2wd^2} \quad (1)$$

where F is the applied force at fracture, S the span, and w and d are specimen width and depth.

Fracture toughness (K_{IC}) was measured using standard single-edge notched beam (SENB) specimens under mode I conditions. SENB specimens were loaded to fracture to determine the fracture toughness of the materials. The size and dimension of the specimen is shown in Fig. 3. The notch was introduced by first cutting a notch with a diamond saw, then generating a pre-crack by gently tapping a fresh razor blade at the base of the notch. The size of the original crack was $0.45W < a < 0.7W$. The specimen was tested at a constant 0.5 mm/min displacement rate until fracture, and 10~15 samples for each composition were tested. Fracture toughness (K_{IC}) was calculated using:

$$K_{IC} = Y\frac{3PS\sqrt{a}}{2BW^2} \quad (2)$$

where P is the critical load, B the thickness, W the width, S the span, and Y is defined as:

$$Y = 1.93 - 3.07\left(\frac{a}{W}\right) + 14.53\left(\frac{a}{W}\right)^2 - 25.11\left(\frac{a}{W}\right)^3 + 25.80\left(\frac{a}{W}\right)^4 \quad (3)$$

Fractured specimens were examined by light microscopy (Keyence VHX-600). Fractured specimens were rejoined using adhesive tape to ensure mutual contact of the crack surfaces, then heated according to the following schedule: (a) heat to 200 °C and hold for 1 h and (b) heat to 220 °C and hold for 1 h. After heat treatment, the K_{IC} of the specimen was measured using the same test procedure used for the control samples. Then the self-healing efficiency (η) was calculated using Eq. (4) [32]:

$$\eta = \frac{K_{IC\ healed}}{K_{IC\ origin}} \quad (4)$$

where $K_{IC\ origin}$ is the fracture toughness of the original specimen and $K_{IC\ healed}$ is the facture toughness of the specimen after healing.

The re-bonding area is calculated using an image processing code (MATLAB). The relative re-bonded area (RRBA) is taken as the fraction of the total available fracture surface that is bonded, and is defined as RRBA = A_b/A_t, where A_t is the total fracture area available for bonding and A_b is the bonded area.

Dynamic mechanical analysis (DMA) was performed using a single cantilever beam clamping setup (TA Q800 DMA) between 30 and 350 °C using a heating rate of 3 °C/min at 1 Hz. Sample dimensions were 35 mm × 10 mm × 2 mm. The glass transition temperature (T_g) was determined from the peak temperature in the tan δ–temperature plot.

The thermogravimetric (TGA) analyses were performed from 30 to 800 °C at a heating rate of 10 °C/min using nitrogen flowing at 50 ml/min (TA Instruments SDTQ500).

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